DEFECT PRODUCTION IN SINGLE CRYSTALS RESULTING FROM ION BOMBARDMENT

by

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Prepared for

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

29 August 1969

GRANT NGR 36-019-001

X RAY PHYSICS LABORATORY
Hiram College
Hiram, Ohio 44234

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I   INTRODUCTION AND SUMMARY

Contained in this report is a summary of the progress made
during the time period from July, 1968 through June, 1969 on the
work supported by the National Aeronautics and Space Administration
to investigate the damage produced on the surface of metal single
crystals during ion bombardment using x-ray methods. This report
covers two semi-annual periods since equipment delays prevented
adequate progress during the period July through December, 1968 to
justify a report.

II   SINGLE CRYSTAL DAMAGE STUDIES

Ultra High Vacuum System

The vacuum system as supplied by Varian[1] has certain de-
ficiencies which are described in a previous report.[2] The primary
problem is that the vacuum specification in the x-ray chamber has
not and will not be met even with the addition of the 15 1/S pump.
The tests on the rotary feedthrough will be described below. Thus
due to the system deficiencies and the nine month shipping delay
Hiram College was finally successful in a renegotiation of the
system price. The system was paid for on February 11, 1969.

Unfortunately the vacuum system has not provided the only
equipment delay. As described in previous reports[3] the vacuum leak
in the ion gun became more serious and finally the ion gun needed
extensive repair. One of the electrical feedthroughs in an octal
feedthrough developed a leak and many attempts to repair it using
Torr Seal[4] were unsuccessful necessitating replacement of the com-
plete octal feedthrough. This repair work[5] was done at NASA Lewis
Research Center and took six months primarily due to slow delivery
of the replacement octal feedthrough. After this repair work the
ion gun was again mounted on the system on January 2, 1969 and sub-
sequently another leak was discovered, this time around the leak tube.

Figure one shows the octal socket and the leak tube feedthrough. This leak again could not be repaired using Torr Seal at the leak tube feedthrough which was located in a recessed hole. The ion gun was dismantled and evidently the leak tube feedthrough had developed a leak previously as it was sealed with soft solder. After thoroughly cleaning the part to be soldered (both were stainless steel) the feedthrough was repaired and the ion gun was mounted on the system for a vacuum leak test. With the ion gun mounted on the system the base pressure is 5×10^{-9} Torr with no further evidence of leaks. This pressure will be adequate to proceed with the bombardment study. The ion gun was placed back into service April 25, 1969.
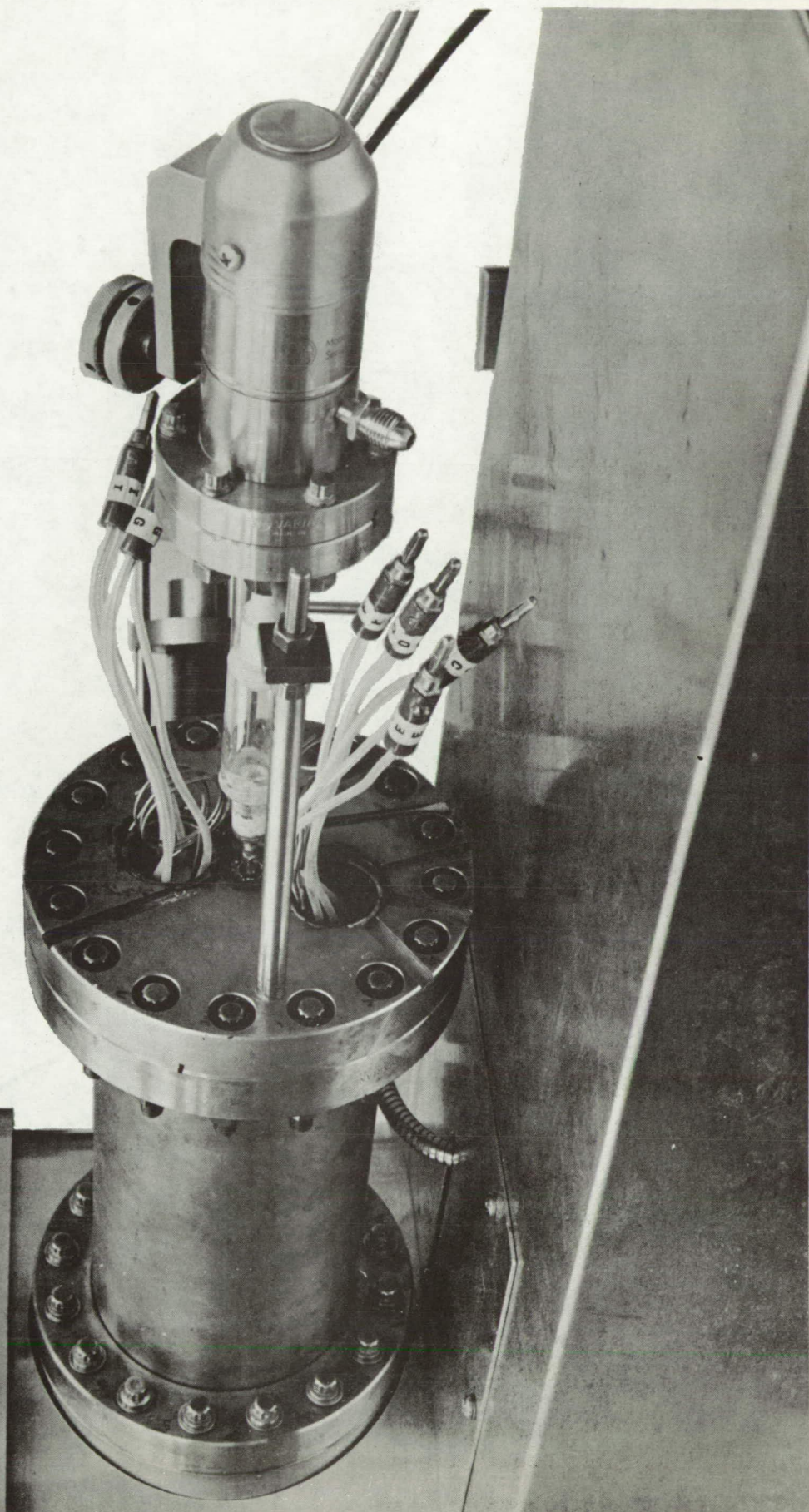
Since April the gun has operated satisfactorily for approximately 69 hours of sputtering time. The procedure used to obtain the discharge in the ion gun is outlined in Table 1. The three hour warm up on the magnetic field coil is necessary to establish thermal and vacuum equilibrium conditions; otherwise continuous adjustments to the coil are required.

TABLE I

Turn up Procedure for Ion Gun

1. Outgas magnetic field coil (@ 8A) and filament (@ 12A) for 3 hours prior to run.
2. Set anode voltage to 60 V.
3. Adjust leak rate of argon to $2-3 \times 10^{-6}$ Torr.
4. Turn on high voltage power supply to 900 V for screen voltage.
5. Set acceleration voltage to 760 V.
6. Decrease magnetic field current to about 4 A to obtain discharge.
7. Then optimize the discharge by adjusting filament, magnetic field current, screen voltage, and leak rate.

FIGURE 1
ION GUN

Some typical operating parameters are filament current, 9.6 A; screen voltage, 800 V; acceleration electrode voltage, 760 V; magnetic field current, 5.2 A; anode current, 390 mA; anode voltage, 60.V; beam current, .48 mA; and crystal current, 125 μA. Figure 2 shows a schematic of the ion gun with all the parameter meters listed above. A Heathkit[5] strip chart recorder is used to continuously monitor the ion beam reaching the crystal. A full scale reading of 125 μA is obtained using a 2 KΩ resistor in parallel with the recorder input. The total beam exposure on the crystal is found by adding up the currents at 1 minute intervals and expressing the result in ion current x time or Coulombs. The crystal beam current stability depends critically upon the pressure range, filament current, and magnetic field current. Fluctuations from 110 μA to 125 μA are not uncommon.

The Varian ion pump apparently develops an "argon instability" in the pressure range around 5×10^{-6} Torr and begins a pressure cycling up and down which usually results in the pump shutting off, i.e. the pressure rising above 1×10^{-4}, unless the argon leak rate is reduced. This cycling usually lasts from 5 to 30 minutes before shutdown occurs. Of course this instability causes problems with the ion beam. Attempts to hold the pressure using only the TSP, i.e. turning off the ion pump have not been successful. If the pressure is kept below 5×10^{-6} Torr, the pump instability usually does not occur.

The Argon gas is of a research grade purchased from Air Products and Chemicals, Inc.[6] The specifications for the gas are listed in Table 2. The gas is delivered to the leak valve[7] at 2-3 psig.

During the delay with the ion gun repair, work proceeded on checking out the rotary feedthrough in the x-ray vacuum chamber and determining a good annealing geometry in the x-ray chamber. The rotary feedthrough test will be described in the next section along with the interface unit test on the double crystal spectrometer. The annealing circuit is shown in Figure 3. For these tests a copper single crystal[8] was mounted on the sample holder. This crystal was 1 inch in diameter and 1/4 inch thick. Thus an indirect heating method (electron bombardment) was used. At 1800 V and 50 mA the annealing temperature of 700°C
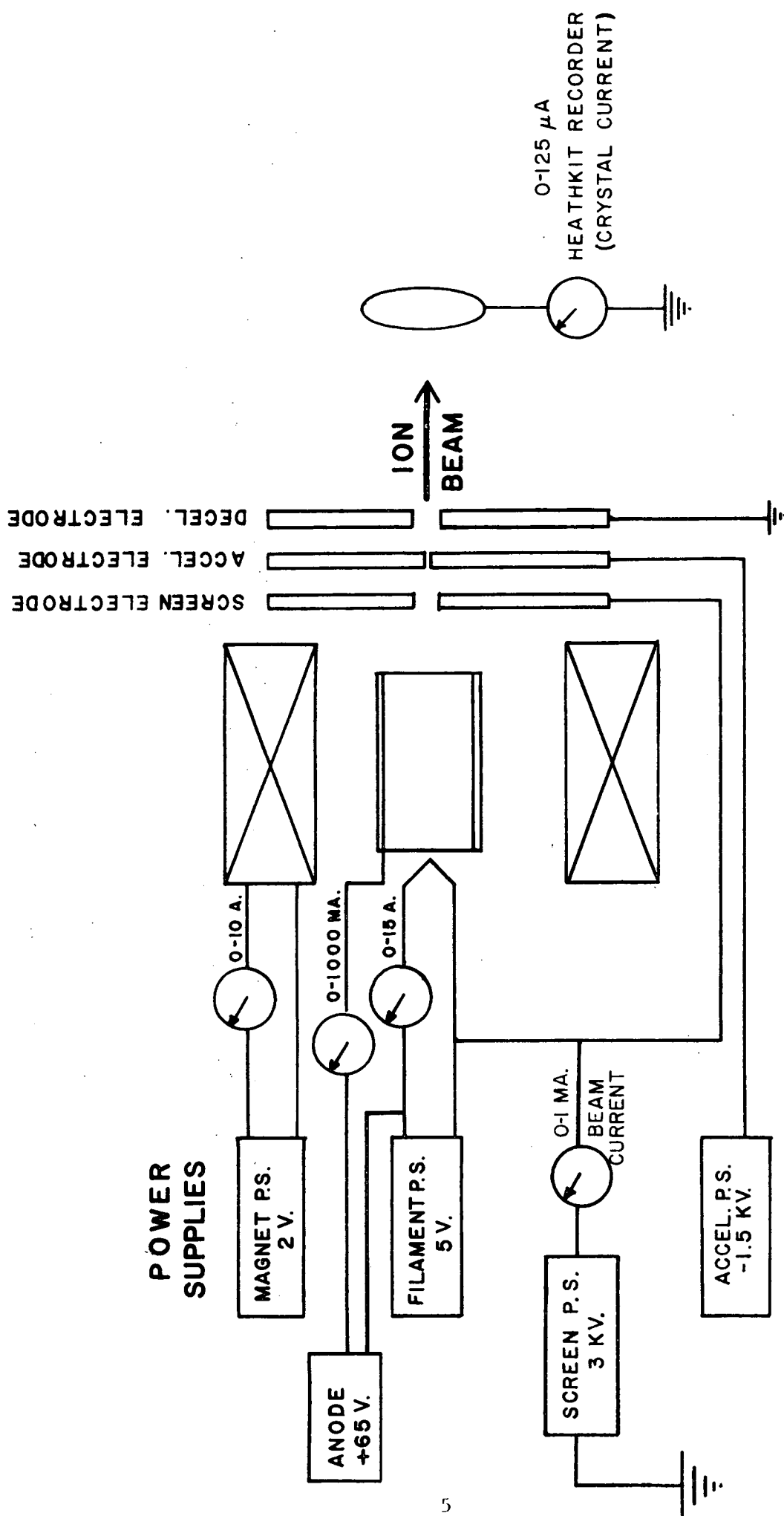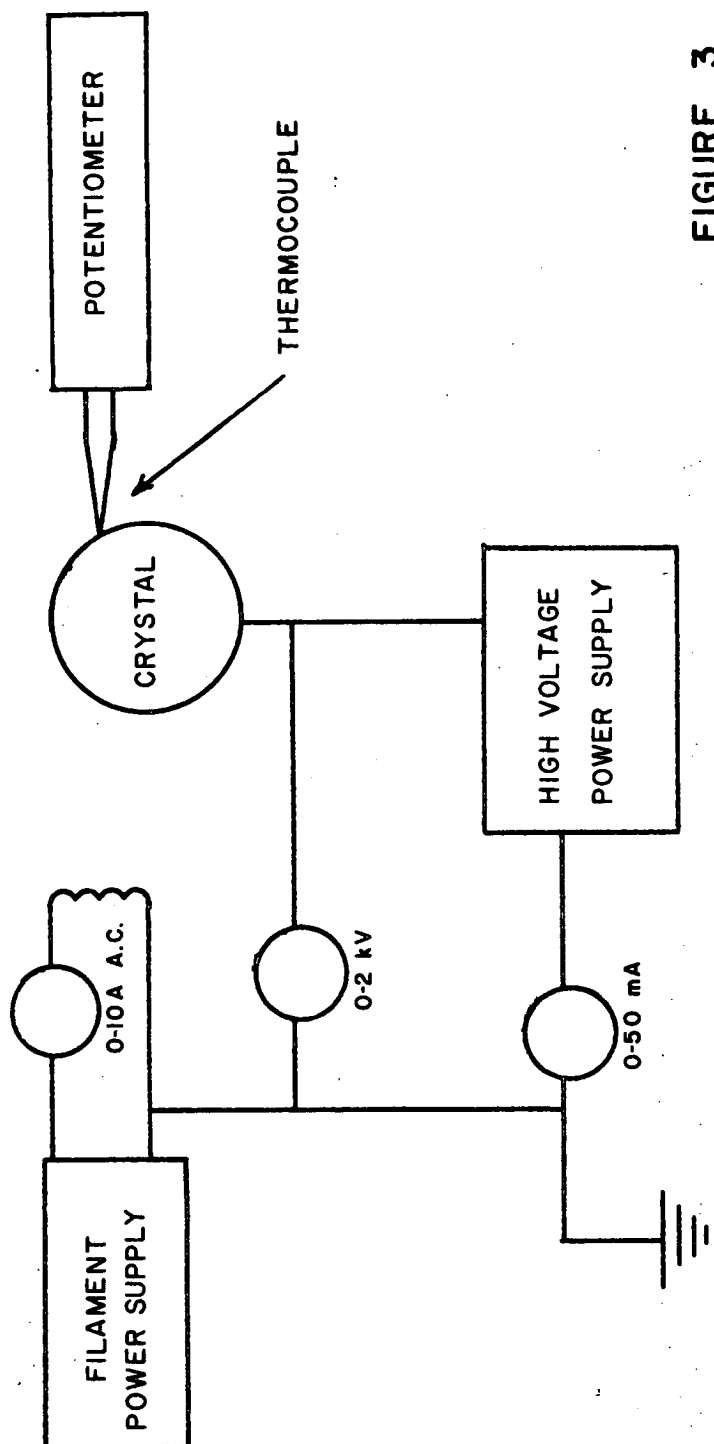
FIGURE 2
ION GUN SCHEMATIC

FIGURE 3

ELECTRON BOMBARDMENT
ANNEALING CIRCUIT

POTENTIOMETER

THERMOCOUPLE

CRYSTAL

HIGH VOLTAGE
POWER SUPPLY

FILAMENT
POWER SUPPLY

0-10A A.C.

0-2 kV

0-50 mA

was reached in about five minutes with the vacuum staying at 1×10^{-7} Torr. The x-ray chamber geometry and feedthrough has been described in detail previously.[9] Unfortunately during the several operations of bolting and unbolting the 8 inch flange on the x-ray chamber a small leak developed in the weld of the Beryllium window to the chamber walls. So far the leak has been repairable using Torr Seal.

TABLE 2

Analysis of Argon Gas

COMPONENT		AMOUNT
Oxygen	0.5	Molar ppm
Nitrogen	1.0	Molar ppm
Hydrogen	<1.0	Molar ppm
Carbon Dioxide	<0.5	Molar ppm
Carbon Monoxide	<1.0	Molar ppm
Nitrous Oxide	<0.1	Molar ppm
Methane	<0.5	Molar ppm
Acetylene	<0.05	Molar ppm
Total Hydrocarbons	<1.0	Molar ppm
Water	0.15	Molar ppm
Water	-125°F	Dew Point

Double Crystal Spectrometer

The high voltage power supply for the x-ray tube on the double crystal spectometer as described previously[10] could not be modified to provide satisfactory current regulation. The original control unit was replaced with a solid state version with no significant improvement. The use of the power supply designed for the rotating anode x-ray tube[11] was also unsatisfactory primarily due to high voltage cable connections. After a minor fire with this

arrangement it was decided to purchase a new power supply. The new power supply[12] was installed May 23, 1969 and, after installing a custom high voltage connection, has operated satisfactorily. The cost of this new unit was shared with the college since although the power supply was necessary for the x-ray work, some of the x-ray cameras and attachments will be used in the instructional program of Hiram College.

During the period from August to November, 1968, attempts were made to obtain a double crystal topograph.[13] Although several types of film and long exposure periods (up to 48 hours) were used these attempts were unsuccessful. The positioning of the film in the x-ray beam was also a problem. Additional work will be performed on this problem.

The check out tests for the rotary feedthrough in the x-ray chamber and the interface unit[14] for mounting the x-ray chamber on the double crystal spectrometer were performed in December, 1969. These tests consisted of determining the precision of the rotary feed-through resettability after an 180° rotation and determining the pre-cision of repositioning the x-ray chamber on the interface unit. To position the x-ray chamber on the double crystal spectrometer so that the quartz crystal was in proper x-ray alignment it was necessary to remove the 8 l/s ion pump, the viewport, and the $1\frac{3}{16}$ straight through valve. Then by mounting a mirror on the face of the crystal so that it extended beyond one end of the crystal it was possible to use a Gauss eyepiece and telescope to adjust the crystal orientation quite closely to the x-ray position. The translation adjustment was made using a dial gauge contacting the mirror. Then the mirror was re-moved and the final orientation was determined using x-rays. Once the peak position was found and the appropriate tilt adjustments[15] were made the chamber was removed and replaced a total of seven times. The change in the position of the peak of the quartz (200) rocking curve was less than ± 2 seconds of arc. The rotary feedthrough was then tested by rotating the crystal through 180° and then back against the stop a total of seven times. The test performed with the crystal in air in-dicated a precision of ± 11.5 seconds of arc and with the chamber
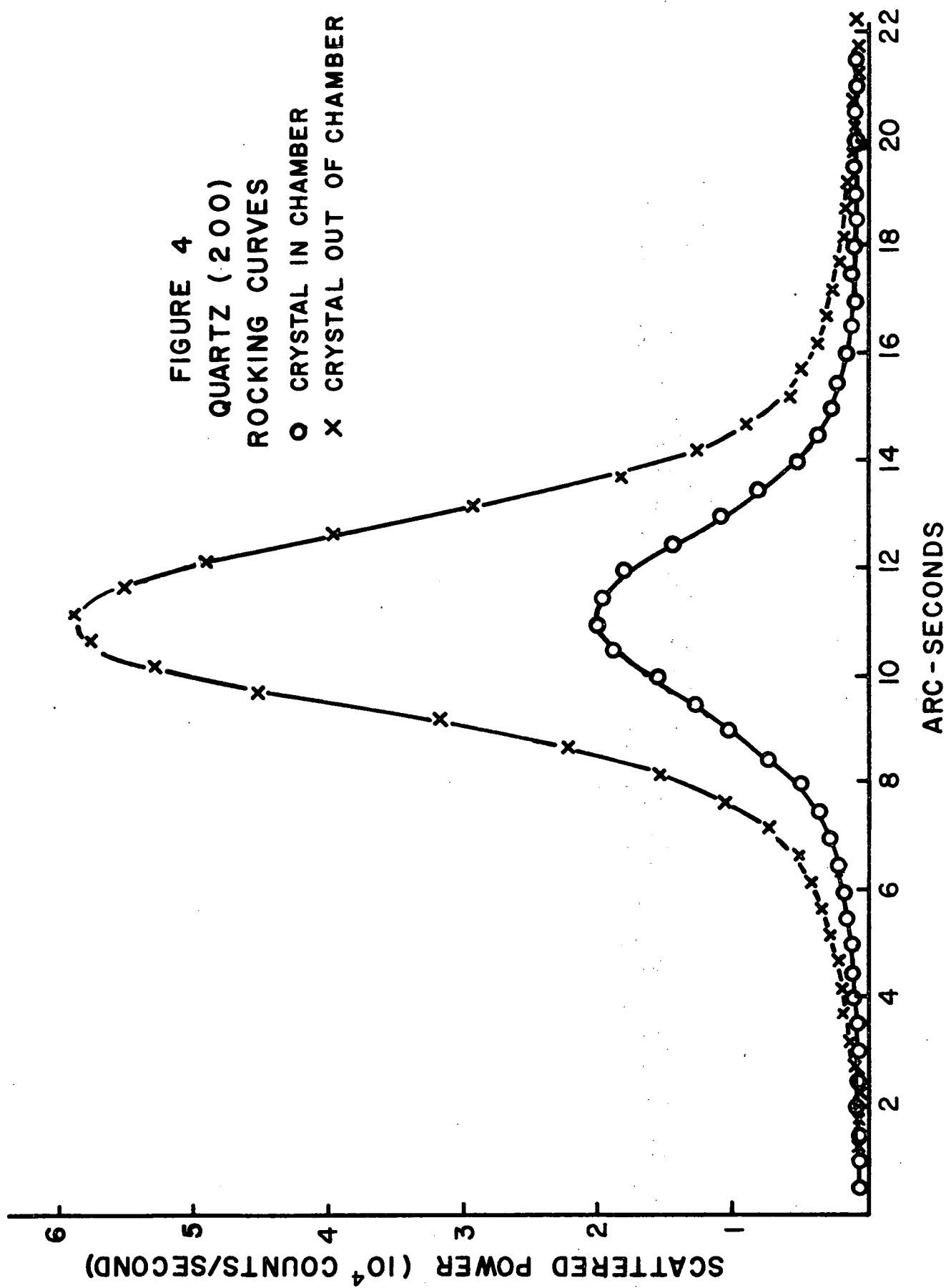
evacuated the resettability was ± 8 seconds. With the chamber re-
assembled for evacuation a counterweight of 6 kg located about 16
inches from the chamber was necessary. Thus the design of both the
rotary feedthrough and the interface unit appears to be within the
original specifications.

The quartz crystal was used in the chamber for the above
checkout since it has an extremely narrow rocking curve and thus was
quite sensitive to small changes in the mechanical mounting and crystal
rotation. Figure 4 shows a quartz (200) rocking curve for the crystal
both in and out of the chamber to illustrate the effect of the Bery-
llium window on the diffracted x-ray beam.

The automation of the data taking process on the double crystal
spectrometer was described earlier.[16] This arrangement has proven to
be quite satisfactory during the past year and has been reported in
the literature.[17] A recent improvement has been the use of the PIP-400
in the multiscale mode to record the rocking curve data so that easy
comparisons of successive rocking curves can be made. The PIP-400 has
three data output options: photograph of cathode ray display, x-y re-
corder output, and digital readout into a 33ASR Teletype page printer
and paper tape punch. For this purpose up to four rocking curves can
be stored and overlapped for easy comparison before readout, usually
by photograph. The PIP-400 is an option in addition to the regular
readout of data through the ORTEC 432 and the other Teletype unit.

III   RESULTS

Preliminary data have been obtained on both copper and germanium
crystals. These crystals have been through a sputtering and annealing
sequence along with the appropriate rocking curves. The crystal has
been placed in the twelve inch vacuum chamber approximately four inches
away from the ion gun. After sputtering the crystal is removed from the
vacuum chamber and placed in the standard sample holder on the double
crystal spectrometer. The crystal orientation in the sample is carefully
preserved from one rocking curve to the next by using lines on the crystal
edge and surface gauge pointers.

FIGURE 4
QUARTZ (200)
ROCKING CURVES
O CRYSTAL IN CHAMBER
X CRYSTAL OUT OF CHAMBER

SCATTERED POWER (10^4 COUNTS/SECOND)

ARC-SECONDS

The copper single crystals[8] were grown by the Czochralski technique, polished, strain annealed, and oriented to (111). The matched crystal technique[18] is used for these studies. Crystal A, the crystal nearest the x-ray tube, is selected so that its lattice planes are as parallel as possible to the planes of crystal B, the crystal to be analyzed. For copper (111) in crystal B, a quartz crystal in the (200) reflection is used in position A. This combination not only has a close match on lattice spacings (2.081Å for copper vs 2.128 Å for quartz) but also the width of the quartz rocking curve (∼4 sec) is much narrower than the copper rocking curve (1100 sec) which makes the curve separation problem much simpler.[19]

Figure 5 shows the copper (111) rocking curve before and after sputtering with 1500 V Argon ions for 15 hours at 50 µA, a dose of about 3 Coulombs for the one inch diameter crystal. Only part of the crystal face was in the ion beam but rocking curves in the two regions were the same. During this rocking curve and sputtering sequence, the copper crystal was observed to take on a double-peaked appearance as shown in Figure 6. Many tests were performed to check the spectrometer and crystals to determine the cause of the double peak. When it was finally determined that the crystals were producing the effect and not the spectrometer the crystal supplier was contacted. Apparently crystals grown with this technique sometimes undergo slippage. The amount of slippage for the copper crystal was found to be about 40 minutes of arc. Venetron now offers crystals grown by the Bridgeman technique and four new copper crystals have recently been obtained.

By using a narrow beam so that only a very small region of the copper crystals were examined it was possible to continue using the old copper crystals during delivery of the new ones. Annealing the copper crystal at 750°C for thirty minutes produced no change in the rocking curve.

FIGURE 5
COPPER (III)
ROCKING CURVES

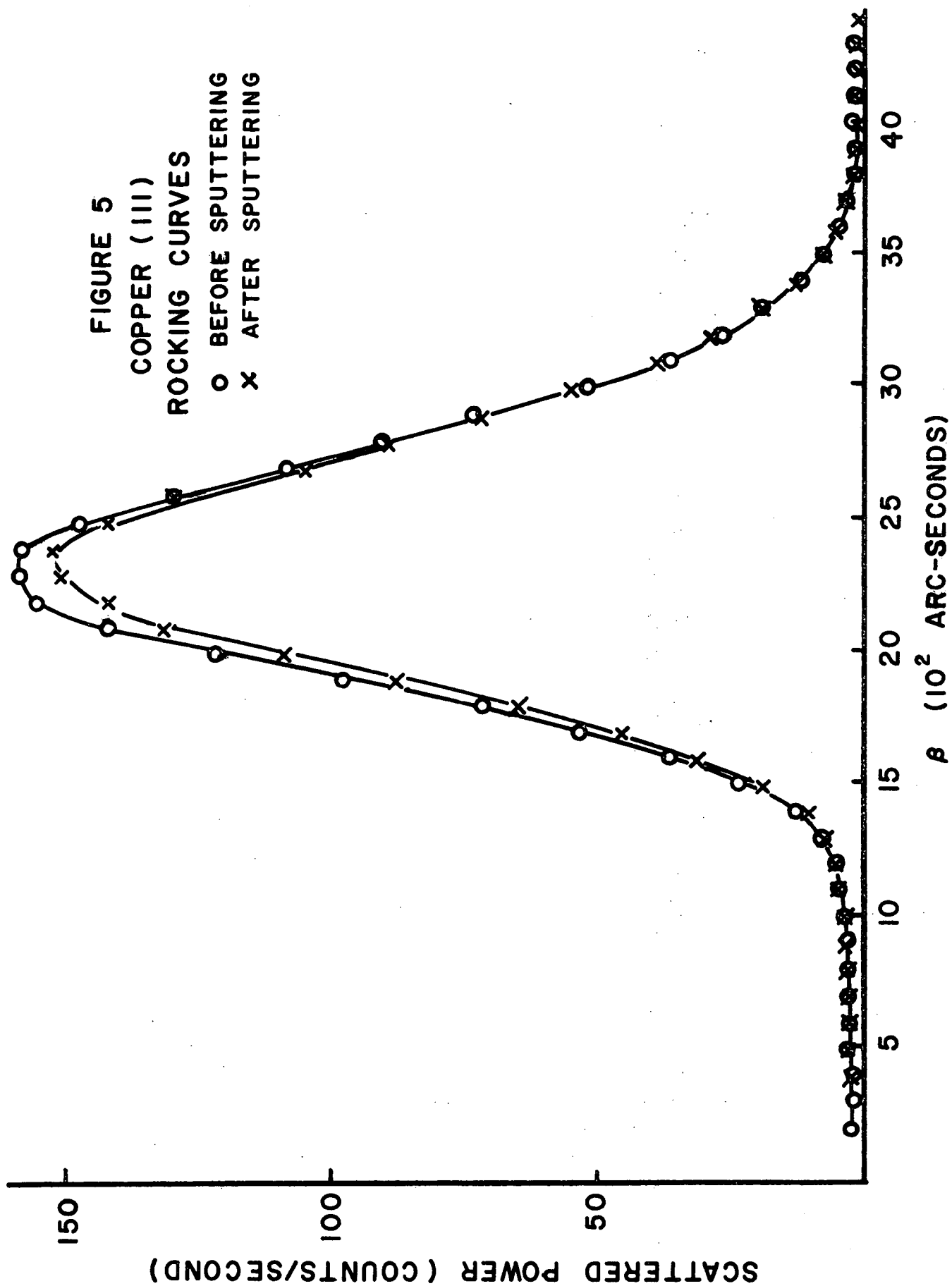O BEFORE SPUTTERING
X AFTER SPUTTERING

SCATTERED POWER (COUNTS/SECOND)

β (10^2 ARC-SECONDS)

12

FIGURE 6
COPPER (III)
ROCKING CURVE
(DOUBLE-PEAKED)

13

TABLE 3

Preliminary Damage Studies of Germanium

PROCESS	COMMENTS	HALF WIDTH
Rocking Curve		22.2 sec
Sputter	1.0 Coulombs	
Rocking Curve		21.6 sec
Anneal	100 minutes at above 450°C	
Rocking Curve		22.4
Sputter	2.5 Coulombs	
Rocking Curve		21.4
Sputter	1.2 Coulombs	
Rocking Curve		21.8

The germanium single crystals were also grown by the Czochralski technique.[8] They were one inch in diameter by one-quarter inch thick, polished, strain annealed, and oriented to (111). No quartz reflection spacing was found to be useful for use with the germanium crystal to utilize the matched crystal technique so a second germanium crystal was used as crystal A. The sputtering, annealing, and rocking curve sequence is summarized in Table 3 above. There appears to be no apparent increase in half width of the rocking curve for germanium with a fairly severe dose of ion bombardment.

Recent work on low energy ion bombardment damage in germanium[20] indicates that with 1000 V Argon ions the damage effects saturated with an ion dose of 1×10^{17} ions/cm^2. In addition the damage should penetrate approximately 25 layers, i.e. 50 Å. The dosage attained at Hiram College was 2.5×10^{19} ions/cm^2 for 2.0 Coulomb dose over the face of the 1" diameter crystal assuming singly charged ions. Due to room temperature fluctuation the precision of the half width measurement is ± 0.3 sec as determined from taking a series of rocking curves without repositioning

the crystal. Attempts to reduce the temperature effect on the spectrometer
precision will continue but since the spectrometer is automated to mini-
mum step sizes of 0.5 sec and the mechanical precision of the micrometer
is only good to 0.2 sec the above value of 0.3 sec is probably about as
good as can be expected.

IV   RECOMMENDATIONS AND PROBLEMS

In spite of the difficulties to date, eg. delayed delivery of
custom equipment, lack of local machine shop facilities for repair, etc., a
fairly effective x-ray research program has been developed and set up at
Hiram College. The equipment is now all apparently operational and the
main problem is enough time to complete more of the proposed work. The
research schedule is now about where it should have been last year at
this time. Performing such a research task at a small college has been
a learning experience in management techniques as essentially all fabrica-
tion of equipment must be done elsewhere with the attendant delays, nec-
essary modifications, and, sometimes modifications due to the item not
meeting specifications. However, the research program has been of great
benefit to Hiram College since the involvement of undergraduate students
working in close cooperation with faculty members on a significant research
problem has contributed to the enhancement of the students' professional
careers.
The preliminary data on copper and germanium apparently show that
the expected line broadening due to ion damage is less than the precision
of the measurement and possibly unmeasureably small. However, the data
needs more analysis particularly in the tail region of the rocking curves.
Adequate computer time has been a slight problem this summer so much of
the data is still being processed. The damage study in the new copper
crystals will begin next as will a renewed effort at obtaining double
crystal topographs as a possibly more sensitive method of determining
ion bombardment damage.

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